# Relationship Between Nickel Content of Soap and Conversion to Polymer in Manufacture of Synthetic Rubber (GR-S)[1]

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COLLABORATIVE research under the Soap Development Program for GR-S of the Rubber Reserve Company revealed that the polyunsaturated fatty components of tallow soap emulsifiers acted as retarders in the emulsion polymerization of GR-S. Reports of this work (3, 6) presented data showing that selective hydrogenation of the fat stock eliminated this difficulty and that spectrophotometric methods (4, 5) of analysis for residual polyunsaturation could be used as a means of production control. Moreover the solution of this problem facilitated conversion of polymerization plants to a continuous process.

In operation of the continuous process for the emulsion polymerization it soon became apparent however that other undesirable substances were sometimes present in the soaps. Variability in plant reactions occurred when some soaps were used which were satisfactory in polyunsaturate content. Although this variability could be overcome to some extent by adjusting the proportion of modifier, there are several valid objections to this adjustment in the practical and economical operation of plants. A study was therefore started in 1946 to determine the cause of this further difficulty.

Rubber Reserve Company plants accumulated data on plant reaction that involved several selected batches of soap having both satisfactory and unsatisfactory characteristics in the continuous polymerization process. Fourteen of these soaps from hydrogenated fats, supplied by four soap manufacturers, with plant polymerization data from three Rubber Reserve Company plants were received by this laboratory for examination.

The soaps were examined spectrophotometrically (4, 5) for polyunsaturated constituents. Table I shows the results of these analyses. Also shown in Table I are conversion as well as amended conversion figures, which have been compensated for variations in polyunsaturated content of the soaps. The corrections introduced for these variations were calculated by use of the formula (3):

$$\text{Drop in conversion} = 1.3 \times \%\ \text{linoleic} + 4\ (\%\ \text{linolenic} + \%\ \text{arachidonic}) \quad (1)$$

Since in the plant conversions are subject to variations with the amount of modifier used, the amended conversion figures in Table I need a further adjustment to reflect a uniform basis of 0.40 part of modifier. This further adjustment is made on the assumption that a 1% drop in conversion is equivalent to a decrease of 0.01 part in charge of modifier. This assumption is reasonably valid for the narrow range of variations in modifier involved. Table I also shows these adjusted conversion data.

Wide variations in the adjusted conversion data indicated that undesirable substances other than polyunsaturates were present in the system. Various considerations indicated that the undesirable activity of certain soaps might be associated with their heavy metal content. Accordingly the soaps were analyzed quantitatively for nickel, copper, and iron. The methods of analysis are described below.

### Method of Analysis

*Preparation of Samples.* Approximately 500 g. of each sample of soap was ground in a mortar to an extremely fine powder. Each powder was then thoroughly mixed by rotation in a glass jar, from which subsequent samples for analyses were drawn.

*Ashing.* Ashing was done under conditions carefully designed to prevent loss of metals. Duplicate 10-gram samples were transferred to 100-ml. platinum dishes. The samples were heated under infrared lamps until thoroughly charred. The dishes were removed and cooled, and 3 ml. of 1:1 sulfuric acid was added. The dishes were rotated in such a fashion that all the charred soap was wetted, and the infrared heating was repeated until sulfuric acid fumes ceased to be evolved and the soaps were carbonized. This required about 14 hours. The carbonized soaps were then ashed in a muffle furnace, where the temperature was raised gradually by 100° increments from room temperature to 600°C.; the 600°C. heating continued for 18 hours (over-night). To destroy the remaining trace of carbonaceous material 3 ml. of concentrated sulfuric acid was added, followed by infrared evaporation and muffle furnace ignition at 600°C. for 6 hours. The ash was taken up with 25 ml. of water, and if it still contained carbonaceous particles, they were destroyed by heating with 30 ml. of aqua regia and evaporating to dryness. The soluble chlorinated ash was taken up and diluted to 100 ml. with water. Aliquots were taken for analysis of the nickel, iron, and copper.

*Metal Analysis: Nickel.* A 25-ml. aliquot of the 100-ml. solution of dissolved ash was analyzed for nickel by the method of Alexander, Godar, and Linde (1). The nickel was isolated from interfering substances by precipitation with dimethylglyoxime, the precipitate was redissolved in hydrochloric acid, and the nickel diethyldithiocarbamate formed was determined with a Beckman spectrophotometer at 385 mμ. Solutions of standards were subjected to the same procedure. The specific extinction coefficient was 64.3.

*Iron.* 25-ml. aliquots of the ash solution were taken for determination of iron; a modification of the method of Hummel and Willard (8) was used. The iron was determined spectrophotometrically after the formation of the ferric salt of 1,10-phenanthroline in

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Spectrophotometric Analysis of Soaps, Plant Conversions to Polymer; Conversions Amended for Polyunsaturation and Adjusted for Modifier; and Analysis of Soaps for Nickel, Copper, and Iron

| Soap No. | Rubber Plant | Soap Mfr. | Polyunsaturated Acids, % (b) | | | | P. I. | 1.3 P. I. | Conversion, % | Amended Conversion, % | Modifier, Parts | Adjusted Conversion, % | Nickel, p.p.m. | Copper, p.p.m. | Iron, p.p.m. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Linoleic | Linolenic | Arachidonic | Conjugated Diene | | | | | | | | | |
| | (a) | | | | | | (c) | (d) | (e) | (f) | (g) | (h) | | | |
| 397 | B | I | 0.19 | 0.02 | 0.00 | 0.08 | 0.25 | 0.3 | 75.3 | 75.6 | 0.424 | 73.2 | 4 | 0.6 | 6 |
| 396 | B | I | 0.51 | 0.06 | 0.00 | 0.19 | 0.68 | 0.9 | 74.6 | 75.5 | 0.424 | 73.1 | 0 | 4.7 | 2 |
| 316 | A | I | 0.16 | 0.00 | 0.00 | 0.09 | 0.16 | 0.2 | 73.7 | 73.9 | 0.45 | 68.9 | 9 | 0.4 | 6 |
| 32 | C | IV | 1.76 | 1.00 | 0.29 | 0.89 | 5.63 | 7.3 | 65.6 | 72.9 | 0.40 | 72.9 | 2 | 16.6 | 149 |
| 517 | C | I | 0.59 | 0.07 | 0.02 | 0.19 | 0.86 | 1.1 | 73.0 | 74.1 | 0.40 | 74.1 | 15 | 1.8 | 5 |
| 340 | A | V | 0.23 | 0.07 | 0.00 | 0.09 | 0.44 | 0.6 | 71.5 | 72.1 | 0.46 | 66.1 | 42 | 1.5 | 45 |
| 137 | A | II | 0.11 | 0.00 | 0.00 | 0.05 | 0.11 | 0.1 | 73.0 | 73.1 | 0.45 | 68.1 | 67 | 1.8 | 39 |
| 338 | A | II | 0.28 | 0.05 | 0.00 | 0.11 | 0.43 | 0.6 | 63.0 | 63.6 | 0.47 | 56.6 | 235 | 5.8 | 1 |
| 395 | B | II | 0.15 | 0.00 | 0.00 | 0.07 | 0.15 | 0.2 | 64.2 | 64.4 | 0.424 | 62.0 | 99 | 0.8 | 13 |
| 25 | C | III | 0.52 | 0.08 | 0.08 | 0.11 | 1.00 | 1.3 | 70.1 | 71.4 | 0.40 | 71.4 | 182 | 2.3 | 100 |
| 27 | C | III | 0.55 | 0.05 | 0.07 | 0.15 | 0.91 | 1.2 | 65.3 | 66.5 | 0.42 | 64.5 | 340 | 2.7 | 112 |
| 305 | A | II | 0.15 | 0.00 | 0.00 | 0.08 | 0.15 | 0.2 | 65.4 | 65.6 | 0.45 | 60.6 | 390 | 2.8 | 21 |
| 344 | A | II | 0.12 | 0.03 | 0.00 | 0.07 | 0.21 | 0.3 | 71.5 | 71.8 | 0.492 | 62.6 | 236 | 3.5 | 23 |
| 398 | B | II | 0.28 | 0.00 | 0.00 | 0.08 | 0.28 | 0.4 | 61.3 | 61.7 | 0.424 | 59.3 | 118 | 3.7 | 29 |

a) Cooperating rubber plants: Goodyear Synthetic Rubber Corp., Houston, Texas; B. F. Goodrich Chemical Company, Borger, Texas; Canadian Synthetic Rubber, Ltd., Sarnia, Ontario, Canada.
b) Spectrophotometric analyses.
c) P. I. (Polymerization index) = % linoleic acid + 3 (% linolenic + % arachidonic acids).
d) Drop in conversion caused by polyunsaturated fatty acids in soap.
e) Conversion to polymer at a viscosity of 50 Mooney; data of rubber plants.
f) Corrected for polyunsaturation.
g) Parts of modifier charged per 100 parts of monomers; data of rubber plants.
h) Calculated for 0.40 part modifier (0.01 part modifier = 1% conversion).

an alkaline medium. The specific extinction coefficient at 505 m$\mu$ was 192.

*Copper.* Copper was determined in the 25-ml. aliquot from which the nickel had been removed; the method of Palfrey, Hobert, Benning, and Dobratz (11) was used. The spectrophotometric method consists of formation of copper diethyldithiocarbamate and uses the specific extinction coefficient of 138 at 435 m$\mu$.

Table I shows the results obtained by these analyses. The order of magnitude of these analyses has been confirmed by polarographic methods (10, 12). It is realized that the reported conversion figures (Table I) were obtained from data on plant operation and that each company may have had some differences in techniques and also may have computed their conversion values somewhat differently. These data nevertheless support the conclusion that, with few exceptions, low nickel content is associated with a high adjusted conversion factor whereas soaps having a high nickel content tend to produce low conversions.

The validity of this conclusion is supported by determining the correlation coefficient of the nickel and the percentage conversion values (9). Thus the coefficient for all nickel values vs. percentage conversion, corrected for modifier and polyunsaturation (adjusted conversion data, Table I), is —0.665, indicating that a relationship exists between these two sets of data. The negative sign, denoting a negative slope, shows that with an increase in nickel concentration the conversion can be expected to decrease. Mathematically it may be stated that with 12 degrees of freedom the probability of obtaining a value of 0.665 or greater, when no correlation exists, is less than 1 chance in 100.

The emulsion polymerization of butadiene and styrene to form GR-S is catalyzed by oxidizing agents, particularly peroxidic compounds. In view of the effect of copper and iron on such oxidizing compounds as peroxides, it seems improbable that nickel would have a greater effect on the reaction than the other two metals. Fortunately calculation of the regression equation for three independent variables (7) offers a procedure for estimating the effect of each.

Using the data obtained for percentage conversion corrected for polyunsaturates and modifier (adjusted conversion, Table I), we obtain the following equation:

$$\% \text{ Conversion} = 68.4 - 0.024 \text{ Ni} + 0.044 \text{ Fe} - 0.127 \text{ Cu} \quad (2)$$

where Ni, Fe, and Cu represent the parts of nickel, iron, and copper per million parts of soap.

Unfortunately it must be recognized that 14 observations are rather few to determine reliably the net relation of any one variable to three other variables, but additional data are not available. Certainly little reliance can be placed in the absolute magnitude of the coefficients of the above equation. Nevertheless this equation indicates that not only nickel but also iron and copper affect the reaction. The positive sign before the coefficient for iron indicates that iron probably favors the reaction whereas the negative sign before the coefficients of nickel and copper indicates that they inhibit it. Moreover the results indicate that copper is considerably more active than nickel in inhibiting the reaction. These indications that copper, iron, and nickel affect the polymerization rate are in accordance with present knowledge (2), and the apparent overwhelming effect of nickel must be due almost entirely to the relatively large proportions contained in most of the samples.

A plot of the adjusted conversion data of Table I versus nickel content of the soaps would obviously not yield a straight line although as stated above a relatively high correlation coefficient between these sets of data was found. However these conversion values can be corrected for the influence of copper and iron by use of equation (2) and the data of Table I so that only the influence of nickel remains. A plot of conversions so corrected versus nickel content of soap is shown in Figure 1. The correlation coefficient between these corrected conversions and the nickel content of the soaps is —0.736, which is appreciably higher than that cited above (—0.665) for the adjusted conversions of Table I. Considerable scattering of points remains and might be expected since data originated from different rubber plants, but a high correlation is evident. There is some indi-

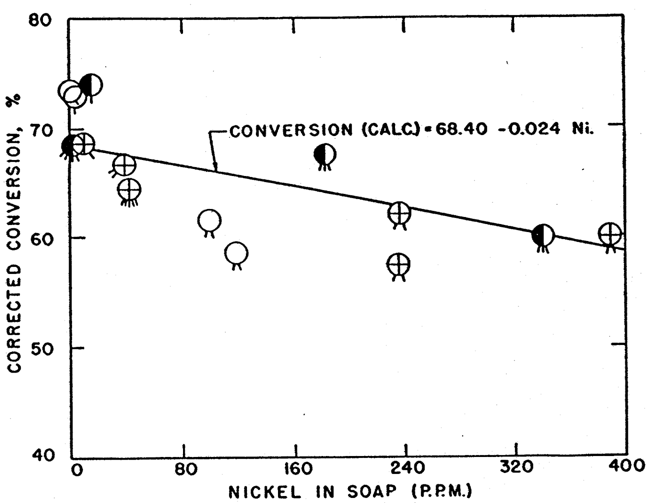


FIG. 1. Observed conversion, corrected for polyunsaturation, modifier differences, and influence of copper and iron content of soap, plotted against nickel content of soap. The circles with crosses represent data originating from rubber plant A, the open circles from plant B, the shaded circles from plant C. The line is calculated from equation (2). Soap supplier indicated by number of radial marks.

cation from inspection of Figure 1 that better individual lines could be drawn through the data of each rubber plant, but application of the z test for homogeneity of population indicates that all data fit the same population.

These findings warrant the conclusion that steps should be taken to prevent contamination of emulsifying agents, to be used in polymerizations, with nickel and other heavy metals.

## Summary


A number of soaps from hydrogenated fat stocks having good and bad characteristics as emulsifiers in plant production of GR-S were analyzed for nickel, copper, and iron. A statistical study of the data on polymerization and metal contents indicated that variability in conversion was associated with variations in the metal content of the soap.


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## REFERENCES


1. Alexander, O. R., Godar, E. M., and Linde, N. J., Ind. Eng. Chem., Anal. Ed., *18*, 206 (1946).

2. Bacon, R. G. R., Trans. Faraday Soc., *42*, pt. 3/4, 140 (1946); Baxendale, J. H., Evans, M. G., and Park, G. S., *Ibid.*, p. 155; Morgan, L. B., *Ibid.*, p. 169.

3. Ault, W. C., Brice, B. A., Swain, M. L., Schaeffer, B. B., and Copley, M. J., J. Am. Oil Chem. Soc., *26*, 700 (1949).

4. Brice, B. A., and Swain, M. L., Opt. Soc. Am., *35*, 532 (1945).

5. Brice, B. A., Swain, M. L., Schaeffer, B. B., and Ault, W. C., Oil and Soap, *22*, 219 (1945).

6. Burke, O. W. Jr., Presented at meeting of American Oil Chem. Soc., Chicago, Ill., November 7, 1945. See also Semon, W. L., J. Am. Oil Chem. Soc. *24*, 33 (1947).

7. Ezekiel, M., "Methods of Correlation Analysis," 2nd Ed., 1941. John Wiley, New York City, Chapter 12, p. 190.

8. Hummel, F. C., and Willard, H. H., Ind. Eng. Chem., Anal. Ed., *10*, 13 (1938).

9. Kenney, J. F., "Mathematics of Statistics," Part I, pp. 170-175.

10. Lingane, J. J., and Kerlinger, H., Ind. Eng. Chem., Anal. Ed., *13*, 77 (1941).

11. Palfrey, G. F., Hobert, R. H., Benning, A. F., and Dobratz, I. W., Ind. Eng. Chem., Anal. Ed., *12*, 94 (1940).

12. Reynolds, C. A., and Rogers, L. B., Anal. Chem., *21*, 176 (1949).